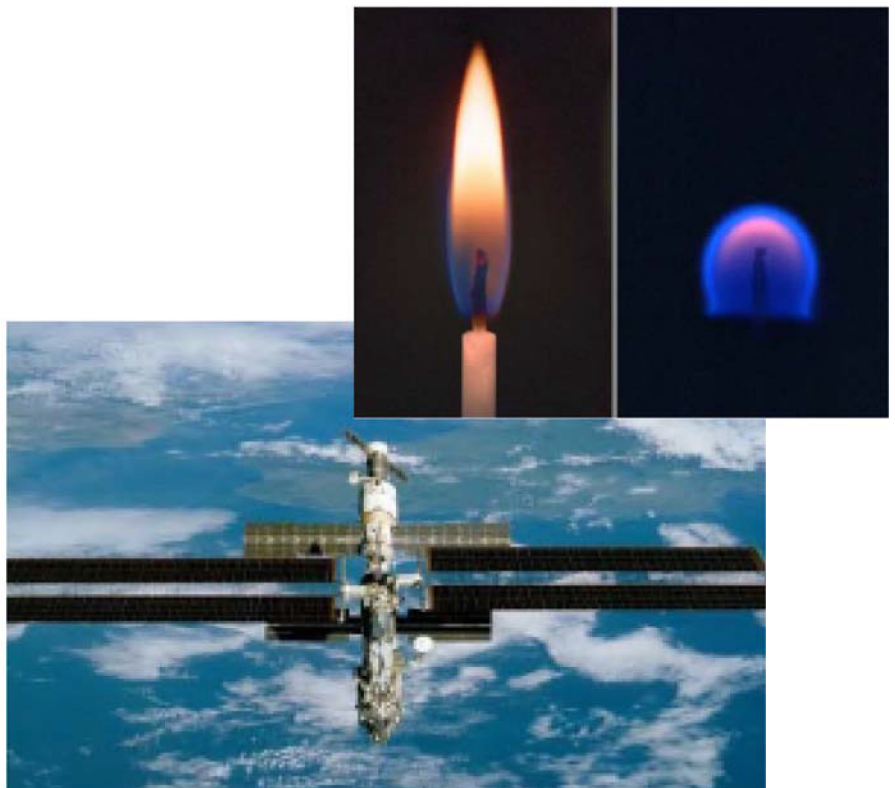




Combustion Products Panel Report

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EXECUTIVE SUMMARY

A panel of non-NASA scientists and engineers with expertise in gas phase analyte sensor development convened in Houston, TX on September 15–16, 2010. The panel evaluated and compared various technologies presented by companies and university research groups and assessed the applicability of each technology for the next combustion products monitor (CPM) on the International Space Station (ISS). Eleven presentations in three main categories were given; these included laser absorption spectrometers, electrochemical and solid state sensors, and colorimetric sensors.

The panel identified laser absorption spectroscopy as the technology with the best prospects for reliable detection of combustion products in a 1–2 year horizon. The technique has a proven ability to measure specific gas phase analytes with minimal cross-species interference.

Electrochemical and solid state sensors have the advantages of small form factor and commercial availability, but they can exhibit false positive or false negative signals for certain compounds, especially HCN. This less-than-optimum selectivity makes these technologies useful only as part of portable “sniffer” units that work in conjunction with optical, rack-mounted sensors.

Laser absorption spectroscopy technology has matured considerably over the last 10 years. It is now possible to develop compact, low-power-consumption sensors based on this approach. It is also possible to integrate other mature sensor technologies with laser absorption spectrometers to develop instruments that can provide a range of useful and reliable data. The time-frame for validating some of these laser-based sensor technologies can be as short as 12 months. The time-frame for implementing validated approaches will depend on the development team. Early involvement of a more-established company with a smaller company or university research group could significantly accelerate development of a sensor suitable for flight.

This panel recommends financial support for research and development efforts in the area of new sensor technologies that will enable more reliable detection of gas phase combustion products. This support should be structured to address key technical risks early in the development phase. Ongoing support should be provided only for technical approaches that will enable fabrication of reliable, compact, and low power consumption sensors. NASA should encourage teaming efforts among large and small entities to expedite sensor development efforts. In addition, NASA should provide a controlled test chamber with appropriate trace gas/fine particle mixtures to test candidate state-of-the-art sensors alongside existing sensors.

The above summary represents the consensus of the panel. The report below consists of panelist comments and recommendations, collected as a single document. The individual comments of each panelist are also available. A table of contents is provided on the next page.

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1.0 INTRODUCTION AND BACKGROUND

In September 2010, NASA held an invited workshop to evaluate the status of technologies available for monitoring combustion products in the environment of the International Space Station (ISS). The workshop comprised 30 minute presentations from developers and manufacturers of monitors that might be used. Presentations were made to a panel of eight non-NASA scientists and engineers with expertise in gas-phase analyte sensor development. The panel had been asked to make recommendations, ranking the candidate monitoring technologies in terms of their current and potential capability. The panel was also asked to identify gaps and point out near-term development path(s) as remedies, including performance improvements that could be achieved with additional investment, as well as potential risks or roadblocks to sensor and system performance improvements.

The presenters were asked to discuss how well their technology would meet a set of desired characteristics and draft requirements for a combustion products monitor (CPM), outlined in Table 1; Appendix A presents the full set of information provided to the presenters. Characteristics and draft requirements were based on several years of experience using the CP monitor currently on the International Space Station as well as on ground-based chemical analysis of samples taken in flight and on the ground. The specifications and requirements are in draft form as of this report and may be subject to trade-off and modification in the future.

Table 1. Desired Analytical Performance for Combustion Products Monitor

Compound	Measurement Range	Resolution
CO	0 – 500 ppm**	1 ppm
HCN	0.4 – 30 ppm**	0.1 ppm
HX*	0.4 – 30 ppm**	0.1 ppm
O ₂	14 – 32%	0.1%
CO ₂	0.05 – 3.0%	0.1% (0.01% < 0.1%)

HX* denotes the total concentration of halide acid gases, HF, HCl and HBr. If a total halide acid gas measurement cannot be provided then the order of preference is the following: HF, HBr, and HCl.

** ppm is parts-per-million by volume at 1 atm.

1.1 The ISS Environment and Needs

The ISS environment poses some technical constraints that influence the evaluation of the various proposed technologies; most of these revolve around ease of use, repair, maintenance, and resupply. The deployed systems must be operationally reliable at all times, must provide unambiguous gas measurements, and must be easily used and deployed in the confines of the space station.

Safe operation of the ISS, and, prospectively, other long duration spacecraft missions, requires a combustion products monitor (CPM) that can assess the time-dependent concentrations of key toxic gases produced by transient fires and oxidative pyrolysis of common onboard materials.

Analyses of prior spacecraft fires and pyrolytic events by NASA toxicologists have identified carbon monoxide (CO) and hydrogen cyanide (HCN) as required target analytes; additional desirable analytes include molecular oxygen (O₂), carbon dioxide (CO₂), hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen bromide (HBr). O₂ is included because combustion and oxidative pyrolysis events can consume oxygen and reduce its concentration in spacecraft atmospheres.

It is important to note that these levels of detection and accuracies must be achieved in a complex ambient gas mixture that may contain most or all of the target analytes as well as significantly elevated levels of many potential interfering species, compared to normal atmospheric air. These include elevated CO₂, methane (CH₄) and molecular hydrogen (H₂), which are often present in normal spacecraft operational conditions. In addition to the target compounds CO, HCN, HF, HCl, and HBr, they may also include a wide range of combustion and pyrolysis products, such as ethyne (C₂H₂), ethane (C₂H₄), and other volatile organic compounds (VOCs), nitrogen oxides (e.g., NO, NO₂ and HONO), and submicron soot/smoke particulate matter (PM). Fire suppression activities may also produce transient high relative humidity.

Additionally, since spacecraft have severe weight, space, and electrical power limits, challenging specifications for these parameters must also be met by the CPM. Furthermore, the CPM must be capable of autonomous continuous operation, requiring only minimal crew time for calibration and maintenance actions. Other requirements include: limited consumable material components, real-time (1 to 5 s) or near real-time (<1 to 5 min.) measurements, quick recovery from saturated measurements, and the ability to operate in microgravity conditions.

The CPM must be an integrated measurement system, not just one or more chemical sensors. It should be capable of continuous rack-mounted operation as well as handheld, battery-powered exploratory measurements. It will require: (1) a sampling subsystem capable of transferring ambient gases into the instrument in both fixed and handheld operations; (2) a sensor subsystem capable of quantifying as many of the target analytes as possible; and (3) a data reduction, analysis, and presentation subsystem capable of processing and displaying data, as well as transmitting data to onboard data collection and transmission devices in real-time or near real-time. The ideal sampling subsystem will deliver ambient air samples to the sensor subsystem, conveying both relatively unreactive gases like CO, CO₂, HCN, and O₂ and “sticky” or reactive gases like HF, HCl, and HBr to and through the sensor subsystem, while not transmitting airborne components like black carbon PM or condensable levels of water vapor that might degrade sensor operations. The ideal sensor subsystem will quantify as many target analytes at desired detection and accuracy levels as possible, with minimal crosstalk between analytes or false positives (or negatives) due to interfering species. The sensor subsystem will also supply any supplementary data such as ambient and/or sensor temperature, pressure, relative humidity, etc. required to analyze analyte concentration data. The ideal data subsystem will automatically reduce, calibrate, analyze, display, and transmit the required data, including evaluated uncertainty limits, within a few seconds of data acquisition.

In addition, the sampling, sensor, and data subsystems must be designed, integrated, and packaged as a single physical unit meeting NASA’s size, weight, power, and durability specifications. The integrated CPM system must be tested, working in collaboration with NASA personnel, employing complex simulated and/or actual combustion/pyrolysis perturbed air samples with known and variable target analytes and compositions that include interfering

species. Finally, candidate CPM systems passing these tests must be space-qualified and then retested to demonstrate adequate target analyte detection and quantification under realistic conditions.

1.2 Toxic Compounds

The CPM has two main functions: (1) sniffing out the location of the source of the combustion gases (fire or overhead source) and (2) monitoring the environment after indications of a fire or other suspect cabin atmospheres (crew-detected odor). In sniffing out the location of the source, the device is used to find the location at which the instrument response is at the maximum reading; for example, in a particular electronics cabinet. When monitoring the cabin atmosphere, a set of readings may prompt the crew to take action.

The desired analytes CO, HCN, CO₂, and HX (halide gases) are toxic gases. NASA has imposed exposure limits in spacecraft for toxic gases. For instance, CO has a 24-hour exposure limit of 55 ppm¹, while HCN has an 8-hour exposure limit of 8 ppm². A fire in a spacecraft or on Earth is an abnormal event where exposure limits are not germane. For instance, one may be exposed to acute levels of toxic gases before protective actions can be taken. To put these safe exposure limits into perspective relative to fire safety on Earth, an examination of International Standard ISO 13571 *Life-threatening components of fire — Guidelines for the estimation of time available for escape using fire data*³ is appropriate.

ISO 13571 considers CO and HCN and the primary asphyxiant toxic gases. Asphyxiation due to oxygen vitiation is not considered unless oxygen concentration falls below 13%. Likewise, narcotic effects of CO₂ are not significant at concentrations typically encountered in otherwise tenable fire environments. However, CO₂ concentrations above 2% increase the uptake of CO and HCN due to hyperventilation. HCl, HBr, and HF are sensory/upper-respiratory irritants. The effects of exposure are determined by the fractional effective dose (FED) for asphyxiant toxic gases and the fractional effective concentration (FEC) for irritant gases. By definition an FED or FEC of 1 is associated with sublethal effects that would render a person of average susceptibility incapable of escaping without assistance. Typically, a FED or FEC of 0.3 is specified to allow all but the most sensitive subjects time to escape.

The specific equations for FED and FEC are provided in the Standard. At an exposure time of 5 minutes, the constant concentrations necessary to reach an FED or the concentration limit for an FEC of 0.3 for CO, HCN, HCl, HBr, and HF are 2100 ppm, 111 ppm, and 300 ppm.

This report is an amalgam of the eight panelist reports. Information sent to presenters and panelists is appended to this report as Appendices A and B, respectively.

2.0 PRESENTATIONS

Several developers and manufacturers of technologies that could be used for combustion products monitoring were invited to participate in the workshop. The list of invitees was made up of companies that had been funded through SBIRs or other NASA contracts as well as other companies, large and small, which manufacture devices that may be suitable. Not all invited companies chose to attend; thus, not all relevant technologies were represented in the presentations.

The proposed technologies included specific chemical detector arrays similar to existing deployed systems, optical methods based on differential absorption, and photoacoustic spectroscopy.

The panel evaluated 11 technical presentations broadly grouped as:

Chemical Sensors: Makel Engineering, Industrial Scientific, Honeywell

Absorption Spectrometers: Fraunhofer Institute, Yokogawa, Block Engineering, Southwest Science

Photoacoustic Spectroscopy: Rice University, Vista Photonics

Other optical technologies: Innosense, Mesa Photonics

2.1 Chemical Sensors (Electrochemical and Solid State)

Chemical sensors have advantage in small package size and low power consumption, and disadvantage with respect to chemical specificity. Cross-sensitivity to the different constituents of fires was considered the main problem with these sensors, because each compound needs its own chemical sensor channel. Also, the need for occasional external chemical calibration was considered an issue with respect to resupply.

The Makel Engineering hardware has space shuttle experience in various rack-mounted configurations. As such, it is expected that their sensors, supporting power supplies, and electronics have sufficient technical viability for micro-gravity. Their proposed instrumentation appears to be sufficiently rugged and sensitive for space flight, but a handheld model that would meet the size and performance criteria is not slated for completion until 2012 or 2013.

The Industrial Scientific entry, MX6 iBrid, is an upgrade of the currently deployed CSA-CP instruments. The MX6 iBrid instrument is configured for either passive absorption or actively pumped mode. The sensors are rugged and meet the performance criteria prescribed by NASA.

The Honeywell presentation did not bring a completed instrument to the table; they have proposed a handheld monitor labeled “Impact Xtreme” that will have a series of important features, not the least of which are an onboard proportional integral derivative (PID) sensor and the ability to communicate wirelessly. The manufacturer indicated that a completed prototype could become available in 2011.

2.2 Absorption Spectrometers

Absorption spectrometers hold the technological edge in compound specificity because of recent developments in a variety of tunable infrared lasers, where a specific absorption feature (vibrational line) of a target gas analyte is chosen that is known to be free of interference from other infrared (IR) absorbing gases, especially water and CO₂. The laser's frequency is swept either across the absorption feature or at least across the shoulder of the feature, and then processed to extract information. Some instruments rely on an integration of the whole feature, where the area becomes the scalable parameter; others rely on various derivatives of the absorption feature as a form of smoothing and peak identification. Typically, each analyte compound requires its own dedicated laser; however, it is possible that absorption features of more than one compound could occur in a single scanned window.

What differentiates absorption spectrometers from optical methods based on direct energy absorption measurement (photoacoustics) is the interpretation and configuration of the analytical signal. Here, the basic method is based on the Beer-Lambert law, wherein the ratio between two signals is processed to achieve an absorption spectrum. The advantage of this technology is that the instrument does not require in-field calibration because the response is dependent only on physical parameters (optical: cross-section at a particular frequency). The choice of a particular instrument within this group is based on specific laser implementation (type, frequency range) and electronic packaging.

The Fraunhofer Institute presented their current instrument capable of CO, O₂, and HCl measurement that uses a multipath cell and commercially available 1.2- to 2.5- μ m lasers that detect overtones. They anticipated development of a handheld instrument satisfying NASA specifications by implementing new laser technology in the 3- to 5- μ m range (for fundamental absorption bands) that will not require the multipath cell; this was expected to take 1 year.

Yokogawa presented an overview of their tunable diode laser absorption spectrometers for combustion monitoring including extractive and long-path applications. These are for industrial rack-mount installations with no attempt made for miniaturization or for portability. The technology relies on existing tunable diode lasers, presumably in the 1.2- to 2.5- μ m range. They had no current plans for developing an instrument for ISS applications but were interested in pursuing such a market niche if there were a market for terrestrial application.

Block Engineering presented their existing technologies in both stand-off Fourier transform infrared (FTIR) and in quantum cascade laser (QCL) measurement instruments. They proposed that the QCL approach has great advantage over FTIR for ISS applications, primarily due to the complexity of engineering required for the FTIR optical bench. Their current QCL instrumentation relies on a frequency range from 6 to 12 μ m, which poses technical challenges because the required gases for NASA applications have fundamental and overtone absorption features in the 1.2- to 5- μ m window. Block Engineering, however, had already implemented handheld instrumentation packages that meet NASA size and weight specifications, and they expected to extend their frequency range below 5 μ m in about 1 year.

Southwest Science started with a brief technical comparison of optical techniques and quickly zeroed in on near-infrared diode lasers (VCSEL) as the best mixture of performance and near-term implementation to address the ISS criteria. The company already fields a series of handheld or miniaturized sensing instruments specifically developed for niche applications including methane sensors for the gas pipeline industry, trace-moisture analyzers for the microelectronics

industry, and oxygen sensors for atmospheric science research. They had already developed rugged packages for stratospheric research for balloons and aircraft, and their proposed implementation for the ISS project was straightforward and adapted existing instrumentation and electronics. Southwest Science proposed using a two-VCSELs package with “jump and scan” spectroscopy for accessing two gases per laser. They would implement a long-path cell to achieve sensitivity criteria.

2.3 Photoacoustic Spectroscopy

The development of high-power tunable diode lasers has brought about a renaissance of photoacoustic spectroscopy (PAS) for trace gas analysis. This is primarily attributed to the scanning ability across absorption features that provides the signal rather than a physical modulation of optical beam power and thus eliminates background “window signal” as an interferant. A fundamental advantage of PAS is that the analytical signal is measured proportionally to absorbed energy; in differential absorption (Beer-Lambert), the analytical signal is detected as a difference between two signals’ similar signal channels, which could introduce additional noise, especially at low concentrations. A fundamental disadvantage of PAS is that it requires external calibration and is somewhat dependent on absolute laser power, although the latter can be circumvented with electronic processing. PAS also requires higher-powered lasers and so increases the overall instrument power requirements.

Rice University presented a discussion comparing PAS with their innovation referred to as quartz-enhanced photoacoustic spectroscopy (QEPAS), in which they use a detector based on tuning fork resonance rather than the traditional electret-style miniature acoustic microphone. This new technology demonstrates two advantages for spaceflight applications with a high signal gain $Q = 10,000$ at 1 atm (signifies extremely low energy loss) and requires only $\sim 2 \text{ mm}^3$ volume for the cell in contrast to $\sim 4500 \text{ mm}^3$ for acoustic cells. They had already demonstrated sensitivity for 16 gases of interest for combustion and other life process interferants and had developed multi-channel prototypes for various applications including exhaled breath analysis. Some potential challenges included the difficulty and cost of high-precision optical alignment, scaling with laser power changes, and potential cross-interferences. The methodology appears to be well-developed and sufficiently rugged for space flight.

Vista Photonics introduced photoacoustic and photodetection wavelength modulation spectroscopy (WMS). They focused on their development of photoacoustic monitors for CO, HCN, CO₂, HF, O₂, and HCl using mid-IR lasers (VCSEL). The current state of development is breadboard configuration with performance that meets the ISS criteria. They expected to be able to construct a package for five gases using five lasers in a configuration of $4'' \times 3'' \times 8''$, (about 1600 cm^3). They expected to require 5 W power; therefore, battery operation is unlikely. A major advantage to this proposed design is the implementation of a self-calibration feature using relative humidity; i.e., including a water spectral feature near each analyte spectral feature to normalize laser power. The methodology appears to be well-developed and sufficiently rugged for space flight.

2.4 Other Optical Technologies

Innosense had developed a series of detection systems that rely on reversible colorimetric chemical substrates coupled with photoemitting diodes they designated the Multi-Analyte Optical Sensor Array (MOSA). The sensors had already been developed for CO, CO₂, and O₂; however, the packaging for ISS specifications had not been completed. They proposed to develop additional sensors for HF, HBr, HCl, and HCN. Their future system for ISS will have low power requirements (battery), on-board data processing and display capabilities, and be the size of a smartphone such as an iPhone or BlackBerry. There was no information on sensor specificity or sensor recovery from high-level exposures.

Mesa Photonics presented an overview of optical techniques and indicated that they were working with some other optical systems. They did not present a specific instrument or plans for developing one. They did, however, present signal processing technology called adaptive baseline correction that may be useful for future implementation of such instruments, in general.

3.0 ANALYSIS: Summary of technical viability and sensor development strengths

3.1 Chemical Sensor Systems

Chemical sensor systems have proven useful and reliable in space applications. They are relatively compact and can be produced as handheld instruments and battery operated. Further development, however, will not likely overcome gas cross-sensitivity issues or the need for external calibration. The chemical sensors themselves are fairly similar across platforms; configuration, packaging, amplifier/controller electronics, and data interpretation differentiate the manufacturers' products. It should be noted that calibration has been shown to be stable over time, and individual chemical sensors can be implemented as small replaceable plug-ins that carry their calibration parameters independent of the host instrument. An important feature of the individual sensors is that they can be manufactured to be plug-replaceable, and their calibration/amplifier electronics reside in the sensor, not in the host instrument.

The chemical sensor technologies presented are similar to those currently used on submarines and on the ISS. However, cross-sensitivities between sensors make detection of carbon monoxide (CO) and hydrogen cyanide (HCN) challenging. For example, the handheld sensor offered by Industrial Scientific, an earlier version of which is currently used on the ISS, utilizes an electrochemical cell (SensoriC HCN 3E 30 F) for HCN detection, and the specification sheet for this sensor (see below) clearly shows that ppm levels of nitric oxide and nitrogen dioxide both generate false negative signals for HCN. As a result, this sensor could falsely show a reading of zero for HCN if it is present in conjunction with NO or NO₂. Since such a combined mixture is likely in the event of a fire, this sensor technology has significant disadvantages as a combustion products monitor.

SensoriC HCN 3E 30 F

CROSS SENSITIVITIES AT 20°C

Gas	Concentration	Reading [ppm]
Alcohols	1000 ppm	0
Carbon Dioxide	5000 ppm	0
Carbon Monoxide	100 ppm	0
Hydrocarbons	% range	0
Hydrogen	10000 ppm	0
Nitric Oxide	100 ppm	-5
Nitrogen Dioxide	10 ppm	-7
Hydrogen Sulfide	20 ppm	0 ¹

Cross species
interferences

1) Short gas exposure in minute range; after filter saturation: ca. 40 ppm reading.

Notes:

1. Interference factors may differ from sensor to sensor and with life time. It is not advisable to calibrate with interference gases.
2. This table does not claim to be complete. The sensor might also be sensitive to other gases.

SensoriC deems the data contained herein as factual, and the opinions expressed are those of qualified experts based on the results of tests conducted. The above data can not be used as a warranty provision or representation for which SensoriC assumes legal responsibility. The data are offered solely for consideration, investigation and verification. Any use of this information is subject to federal, state and local laws and regulations.



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Figure 1. SensoriC HCN 3E 30 F Specifications.

The Navy has tested similar sensors for potential use on submarines⁴⁻⁶ and for fire detection⁷. These studies have shown that HCl sensors lack stability⁵. This technology needs further sensor development for HCN and HX.

It may be possible to overcome some cross-sensitivity issues using multivariate data analysis and an array of sensors. The small size makes the technology suitable for an electronic nose approach using arrays of sensors and pattern recognition. The hybrid photo-diode and colorimetric/chemical sensor combination from Honeywell has a size advantage in that a fully integrated screening device could be packaged within the size of a cell phone.

Solid-state sensors can be very compact, low-mass, and low-power, but they are susceptible to deposition of films from continuous exposure to the atmosphere as well as gradual oxidation or other chemical reactions or physical changes of the transduction components that could degrade their performance. Calibration would always be an issue. The influence of interfering gases such as O₂, H₂O, CO, NO, NO₂, CH₄, and SO₂ on a CO₂ sensor has been reported in the literature, such as O₂ for a CO₂ sensor⁵⁻⁹. Degradation resulting from exposure to ionizing radiation may also be an issue.

The long-awaited ChemFET remains a technology of tomorrow⁸.

The most viable entry for the category of chemical sensors is the MX6-iBrid, because it is ready to deploy.

3.2 Laser Spectroscopy Systems

The advent of various tunable near-IR and mid-IR lasers has made optical absorption spectroscopy an extremely viable technology for specific and relatively small gas-measurement instrumentation. The main technical advantage is that external calibration is not necessary. A minor disadvantage is relative sensitivity; multi-path cells are likely required to achieve sufficient differential absorption at the overtone frequencies currently accessed by the lasers. New laser development at fundamental frequencies may overcome this issue.

Similarly, photoacoustic spectroscopy has benefited from the tunable IR laser advances. The main advantage of PAS over absorption spectroscopy is sensitivity; as such, PAS cells can be made extremely small. One disadvantage is total power consumption, because PAS requires higher-powered lasers. PAS measurement is also influenced by absolute laser-power level. The issue of external calibration, however, is surmountable because there is technology under development that employs adjacent water lines as relative normalization factors for power fluctuations or drift.

Seven different groups presented combustion products monitoring concepts that were based on tunable IR laser spectrometry. The details of the conceptual CPM designs they discussed varied significantly, as did the maturity and current availability of the sensor components they included. However, with the exception of an O₂ analyte measurement, the basic physics of all seven presentations can be captured in a two-by-two matrix based on the spectral regions and detection processes proposed. This matrix is based on the choice of near-infrared (~0.75 to 2.5 μm) or mid-infrared (~2.5 to 6 μm) wavelength lasers and the choice of direct IR absorption or photoacoustic detection (Table 2).

Table 2. Tunable IR Spectroscopy Matrix

Near-IR Lasers	Mid-IR Lasers
Direct-IR Absorption Detection	Photoacoustic Detection

Several types of tunable near-IR lasers have been developed commercially, primarily for telecommunications applications. These lasers tend to be relatively compact, robust, and inexpensive. Some also produce output powers strong enough for sensitive photoacoustic detection, based on sensing the pressure wave created when a pulsed or chopped laser beam is absorbed by gaseous species in an enclosed sample space.

Mid-IR tunable lasers tend to be bulkier, more expensive, and at some wavelengths, more difficult to procure than the more widely used near-IR lasers. However, the vibrational/rotational transitions of most of the combustion product target analytes in the mid-IR are fundamental transitions that absorb light ~10 to several 100 times more strongly than the overtone and combination bands found in the near-IR portion of the spectrum. Because the mid-IR transitions of CO, HCN, and the HX gases are much stronger than their near-IR transitions, shorter absorption pathlengths are required for either photoacoustic or direct-IR absorption detection. In principle, the same is true for CO₂, but there is so much of it in the ISS atmosphere that it is easy to quantify in either wavelength region. The exception, noted above, is O₂, which for symmetry reasons has exceedingly weak vibrational/rotational absorption features at any IR wavelength and is usually detected using a weak electronic transition in the near-infrared.

Both methods of tunable IR laser absorption have attractive features. Photoacoustic detectors are very robust, relatively inexpensive, can be used for laser absorption measurements across very wide wavelength regions, and do not suffer from quantum interference effects that can affect direct photon-absorption measurements that require complex optics. However, photoacoustic detectors require independent calibration. The signal from a photoacoustic detector is directly dependent on the laser power for most common operating conditions, so more powerful lasers, drawing more electrical power, may be required for photoacoustic detection than direct-IR absorption detection.

Direct detection of laser absorption can be quantified by measuring the difference in photons reaching a detector as the laser is tuned on and off a molecular absorption feature with a known absorption strength, as long as the absorption path length and absorption gas sample temperature and pressure are known. However, photon detectors can be more expensive than photoacoustic detectors, especially in the mid-IR region.

The choice of the optimal laser wavelengths and detection method are strongly influenced by the required measurement sensitivity and specificity, as well as the size, weight, power, and cost specifications set for a given monitoring instrument.

The spectroscopic methods are all attractive because they offer selectivity and potential for stable operation, low maintenance, and minimal calibration requirements. However, the technologies are long-term solutions for NASA's application because research and development is required. In the past, high cost and a lack of sensitivity have been issues for spectroscopic methods. Advances in low-cost lasers make these methods very attractive for detection of specific chemicals in a complex background.

An intriguing technical development from Southwest Sciences is the open optical path instrument that they developed for atmospheric research; this is the only configuration proposed so far that would make direct *in situ* measurements of highly reactive gases (e.g., HF). Using an open path is more difficult to implement in an ISS environment; however, the proposed instrumentation could be configured with a Herriott cell option as well.

There was some discussion as to whether HCN could be detected using spectroscopic techniques with currently available lasers. Below is a simulation of 1 ppm CO, 1 ppm HCN, 1000 ppm CO₂, 100 ppm CH₄, and 3% water in two wavelength regions: 1530 to 1540 nm (6494 to 6536 cm⁻¹) (for HCN detection) and 1560 to 1570 nm (6369 to 6410 cm⁻¹) (for CO detection). "No fire" means no CO and HCN. The y-axis is extinction coefficient (in units of inverse cm). The simulations show that is feasible to detect HCN by several of the laser approaches.

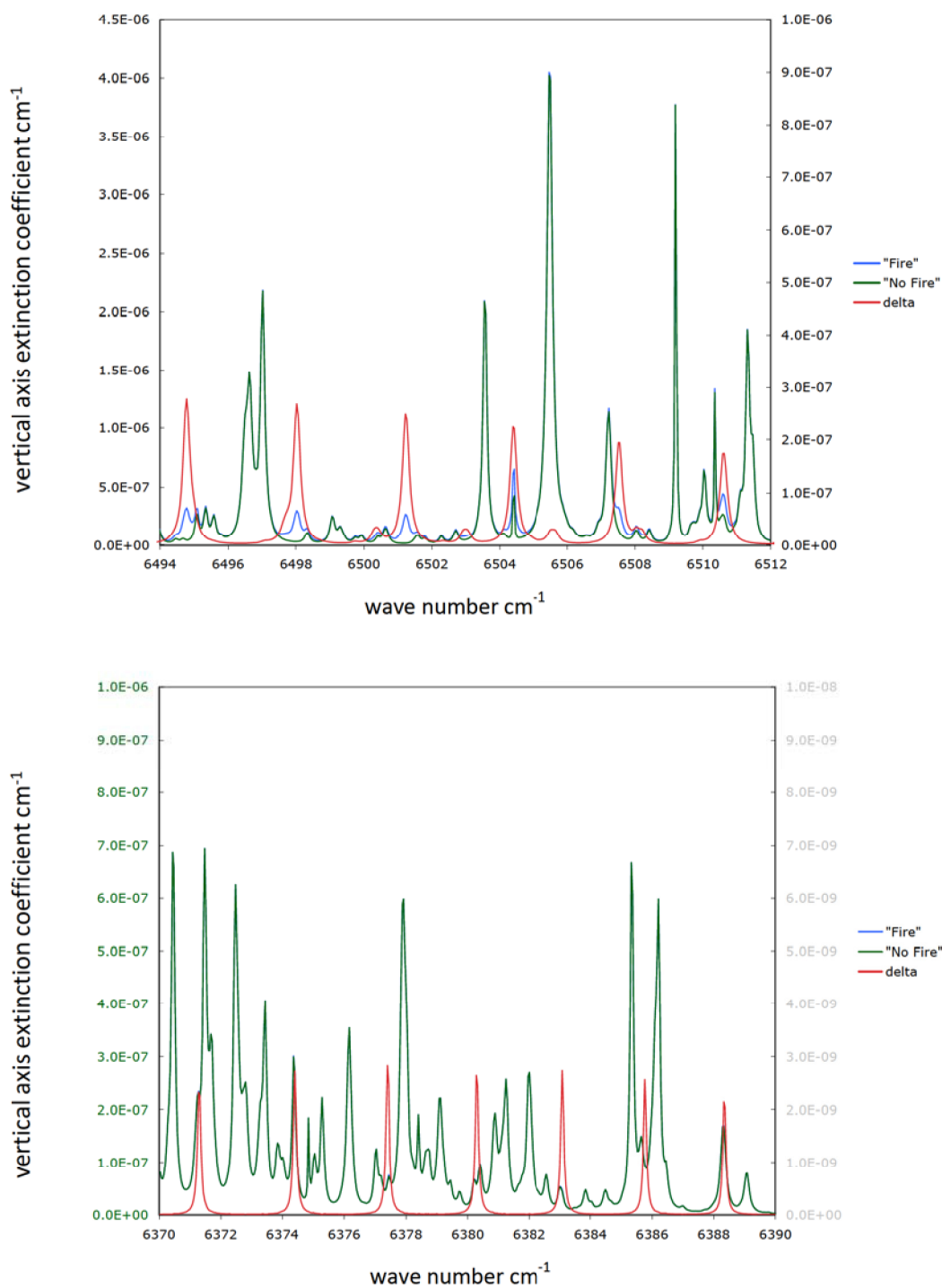


Figure 2. Extinction coefficient in the presence of 1 ppm CO, 1 ppm HCN, 1000 ppm CO₂, 100 ppm CH₄, and 3% water in two wavelength regions.

3.3 Other Methods

The reversible colorimetric methods described by InnoSense require significant development before they are suitable for the ISS. The limited details provided about the sensing mechanisms make assessment of the methods difficult; however, selectivity and long stability are a concern because InnoSense is using redox reactions and relying on buffers to reverse the reactions. It is expected that there will be many potential interferences for each of the sensors and no testing has been done using complex mixtures. The methods as presented are a high-risk solution for this application. Colorimetric methods have been used successfully in the past with specificity achieved using nonreversible chemical reactions such as those used in Draeger tubes.

3.4 Technologies Not Presented

3.4A *Mass Spectrometry and Related Techniques*

Optical detection is limited in the sense that it is exquisitely selective for only a small group of analytes. Emergency scenarios where fire incidents produce combustion products outside the detection envelope of a targeted optical sensor may result in exposure of personnel to other gases not anticipated in the original analyte panel, with unknown toxicological effects. The technology pre-selection conducted at NASA resulted in no responses from companies or research groups developing miniaturized mass spectrometry (MS), ion mobility (IMS), and/or differential mobility (DMS) units. This is not equivalent to saying that none is a viable technology – very small ion-trap-based instruments have been built⁹⁻¹¹.

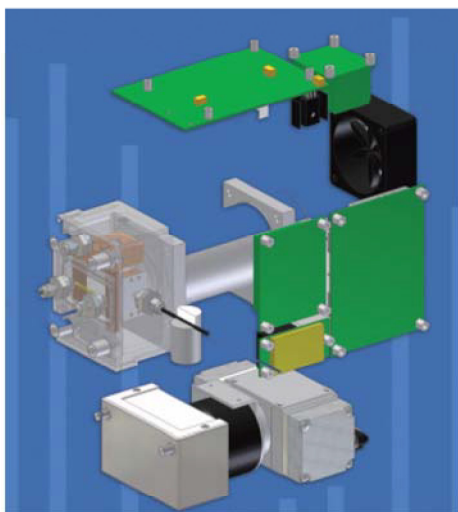
Mass Spectrometry

Most recent developments in the field of portable mass spectrometers have involved miniature ion-trap technology, reviewed by Ouyang and Cooks¹². Mass spectrometers built around ion-trap technology have been shown to meet the size, weight, and power requirements (<100 g, 1 W) for combustion products monitoring¹³. Beam-type mass analyzers, such as time-of-flight (TOF) and sector mass analyzers, are usually much larger than trapping mass analyzers such as quadrupole ion traps (QIT). The linear quadrupole mass filter is also proving to be a popular miniature mass analyzer, and it has been utilized as a single analyzer and in arrays of identical mass analyzers. The original Paul QIT has slowly but steadily evolved into simplified analog designs including the cylindrical ion trap (CIT). Other geometries with higher trapping capacity, such as the linear trap, the toroidal trap, and the HALO trap have also been proposed as alternatives.

The specific problem identified by the panel resides in that simple mass spectrometers cannot distinguish between CO (exact mass=27.9949) and N₂ (exact mass=28.0061), or between CO₂ (exact mass=43.9898) and N₂O (exact mass=44.0010). Resolution of these species at full-width, half maximum requires resolving powers of 2500 and 2150, respectively. Two main avenues exist to avoid these isobaric interferences. The first involves separation prior to ionization using gas chromatography (GC), and the second uses high-resolution mass spectrometry approaches. The characteristics set for the CPM do not favor the use of separation techniques such as GC, indicating that the use of high-resolution measurements in a portable mass spectrometer would be the desirable path. QIT-based mass spectrometers are, in principle, capable of high-resolution measurements in a small, user-selectable mass range, which should make them amenable to CP monitoring applications¹⁴.

For miniaturized mass spectrometers to survive the space environment, components must be reliable and robust. The stability and shelf life of the ionizer used is therefore another variable to take into consideration. Micro-machined silicon emitters coated with diamond-like carbon (DLC) have been proposed as a robust alternative to typical filament emitters¹⁵.

Mass spectrometers generally need to operate under vacuum, often under high vacuum. Possible configurations include: time-of-flight¹⁶, quadrupole¹⁷, and ion-trap designs¹¹; there is an excellent review by Palmer and Limero¹⁸. The advantage of mass spectrometers that are based on ion traps is their relatively small size and weight, which makes them particularly appropriate for NASA applications.



For toxic gases, such as phosgene, ethylene oxide, sulfur dioxide, acrylonitrile, cyanogen chloride, hydrogen cyanide, acrolein, formaldehyde, and ethyl parathion, a 1-minute preconcentration time is required. Detection limits range from 800 ppt to 3 ppm, depending on the analyte. For these particular compounds, a linear dynamic range of 1 to 2 orders of magnitude was obtained over the concentration range (sub-parts per billion to parts per million) for all analytes.¹⁰

Ion Mobility-based techniques

During the past decade, ion mobility (IM) separation approaches have matured into rugged, dependable, field analytical techniques¹⁹. Several types of IM approaches, such as differential ion mobility spectrometry (DMS), traveling wave ion mobility spectrometry (TWIMS), field-asymmetric ion mobility spectrometry (FAIMS), and drift tube ion mobility spectrometry have been reported as successful means of separating ionic species prior to point charge or MS detection. DTIMS, the most common IM approach, is a rapid post-ionization gas-phase separation technique that distinguishes between compounds based on their differences in reduced mass, charge, and collisional cross-section under a weak, time-invariant electric field applied to a drift tube. Mobility (K) is determined from the drift velocity (v_d) attained by ions in a weak electric field (E) in the drift tube, according to the equation, $v_d = K \times E$. The distribution of these signals forms a mobility spectrum, with an ion-mobility band corresponding to each of the unique ionic species. The spectrum is a fingerprint of the parent compound. Due to its ruggedness and atmospheric pressure operation capabilities, over 50,000 stand-alone drift tube IM spectrometers are currently employed throughout the world for the detection of explosives, drugs of abuse, and chemical-warfare agents. It is important to note that IMS operates at atmospheric pressure.

IMS performs analysis in milliseconds to seconds at a minimal cost because there are no column materials and no extensive solvent used for sensitive species separation²⁰. DMS is different than DTIMS in that ions are separated by an asymmetric voltage waveform applied to two parallel plates which causes a net deviation in the ions' trajectory due to the differences in ion mobility at low and high electrical fields. DMS has the advantage over IMS in that it has a higher duty cycle, but a lower resolving power. DMS and IMS do not provide simple ways for identifying observed peaks, but are very powerful as pre-MS separation devices that do not decrease the overall throughput of the measurement. IM-MS portable instrumentation has been recently reported based on the Sionex DMS unit and the Mini-11 platform developed by the Cooks group at Purdue.

The analysis and characterization via IMS are based on differing ionic mobilities through a background or carrier gas rather than simply their differing m/z . IMS units can analyze air, vapor, soil, and water samples; for analysis of volatile components of liquid or solid materials, the volatile components must be introduced to the instrument in the gas phase, requiring sample preparation.

R&D teams working with, or independent of, NASA have created portable IMS and/or GC-IMS systems²¹⁻²³. A new kind of differential ion-mobility spectrometer with reduced volume and weight²²⁻²⁴ was incorporated in the Sionex microAnalyzer™ (however, Scionex is no longer in business). Such systems can be very small and lightweight and the Sionex instrument, which is already under test by NASA personnel, appears well-suited for space applications. Numerous hand-held IMS instruments incorporate drift tubes manufactured by Graseby²⁵. Graseby Ionics, Ltd. has a self-contained IMS that weighs about 2 kg.



Figure 3. Improved Chemical Agent Monitor (Graseby)

The Improved Chemical Agent Monitor (Graseby) is an improvement over the currently fielded CAM. The modular design is less expensive to repair, requires less maintenance, and eliminates depot-level repair now required for the CAM. The ICAM also starts up faster after prolonged storage and is more reliable.



Figure 4. FemtoScan: EVM II instrument uses Graesby drift tubes.

A platform of the IMS/DMS type could offer an interesting complement to an all-optical CPM. Not only could results be validated by two redundant detectors based on orthogonal detection principles, but also unknown VOCs that may arise in a fire event could be simultaneously monitored with the IM-MS unit.

3.4B Raman Spectroscopy

Both traditional Raman techniques²⁶ as well as photoacoustic Raman techniques²⁷⁻²⁹ have been published – the possibility of instruments based on Raman spectroscopy being able to meet size, power, and ruggedness requirements is unknown. Nonetheless, Raman-based instruments for general gas analysis, including N₂, O₂, CO₂, and H₂O should be investigated.

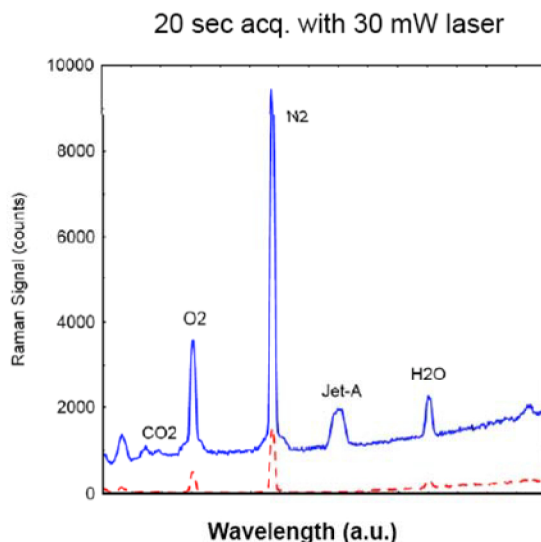


Figure 5. Raman spectra showing N₂, O₂, CO₂, and H₂O taken using a single-pass, fiber-optic system by Q-V Nguyen of NASA GRC³⁰.

Detection of N₂, O₂, CO₂ was demonstrated in 1968 with Raman spectroscopy²⁶. Further work has found that intra-cavity configurations enhance Raman sensitivity^{27, 28, 31}, and photoacoustic Raman spectroscopy (PARS) was demonstrated in the seventies²⁷⁻²⁹. Raman spectroscopy has been applied to the analysis of mixtures of CH₄ in N₂, CO₂ in N₂, and N₂O in N₂ at concentrations near 1 ppm²⁷.

With excitation at 488 nm, the Raman cross-section for CO is eight times smaller than that of CH₄, which should still provide tens of ppm sensitivity for CO detection with little risk of interference. Privalov estimated 10¹³/cm³ (order of 1 ppm) detection of HF at a standoff distance of 1 meter. HCl would also have a larger Raman scattering cross section than CO (lower limit of detection).

Table 3. Sensitivity Limits for PARS Trace Analysis.

Sample	Monitored transition	Buffer gas	E_s (mJ)	E_p (mJ)	Concentration (ppm)	Observed SNR	SNR = 1 limit (ppm)	Laser ^a system
CH ₄	$\nu_1 \leftarrow 0$	N ₂	14.5	50	2	2	1	QR
CO ₂	$\nu_1 \leftarrow 0$	N ₂	18	20	6.3	2.5	2.5	QR
CO ₂	$\nu_1 \leftarrow 0$	N ₂	3.0	9	250	2	125	M
N ₂ O	$\nu_1 \leftarrow 0$	N ₂	27	15	100	5	20	QR
N ₂ O	$\nu_1 \leftarrow 0$	N ₂	≤1.5	10	1400	2	700	M
C ₂ H ₄	$\nu_3 \leftarrow 0$	N ₂	2.4	10	350	2	175(4) ^b	M
C ₂ H ₃ Cl	$\nu_4 \leftarrow 0$	N ₂	3.8	11	360	1	360(9) ^b	M
O ₂	$1 \leftarrow 0 = \nu$	C ₂ H ₄	3.5	9.5	2000	5	400(10) ^b	M

^a QR = high-power dye laser (Quanta-Ray); M = low-power dye laser (Molelectron).

^b The values in parentheses are the anticipated sensitivity limits with the QR system, assuming a typical sensitivity improvement factor of 40× at the higher laser energies.

3.4C Cavity-ringdown Spectroscopy

Because cavity-ringdown spectroscopy³² (CRS) requires a very high-Q optical cavity (extremely high-reflectance mirrors and very low losses, generally, aside from the absorption of the gaseous molecules of interest), any mechanism that degrades the Q also concomitantly degrades the performance of the CRS instrument. This can include “errant” aerosol particles and films that gradually build up on the surfaces of the optics, etc. Other issues to be addressed would be evaluation of possible cross-signals from multiple species and the tradeoff between narrowing the bandwidth of the excitation light source to reduce or eliminate such cross-signals and the accompanying tradeoffs of signal strength and the rapidity with which a mixture of many gases at widely-differing concentrations can be monitored.

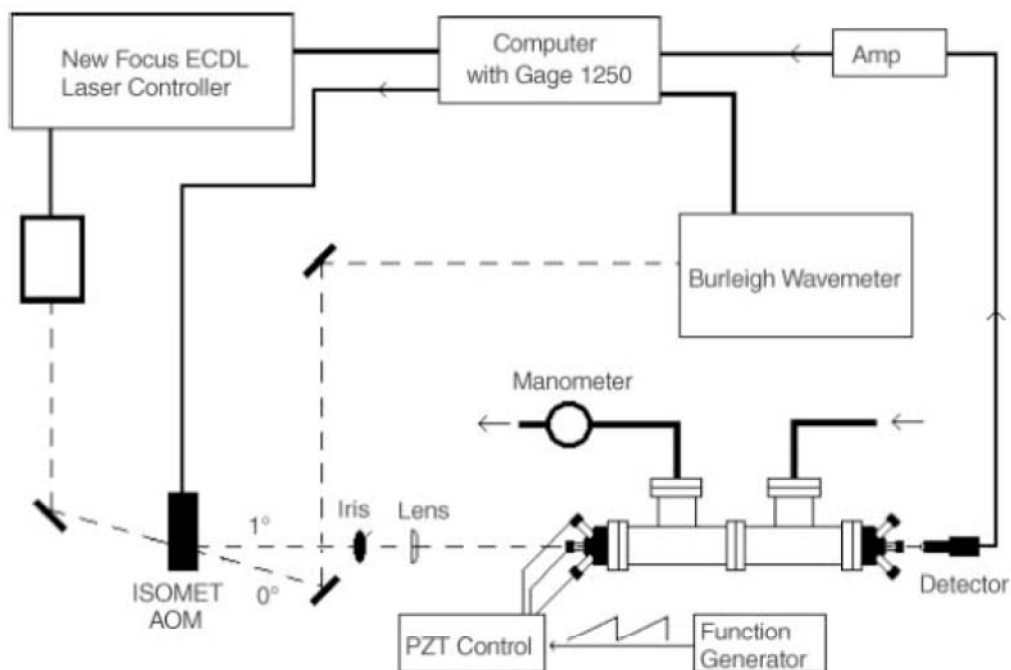


Figure 6. Schematic layout of the experimental set-up.

A continuous-wave (cw), external-cavity, tunable diode laser centered at $1.55\ \mu\text{m}$ is used to pump an optical cavity absorption cell in cw-cavity ringdown spectroscopy (cw-CRDS). Preliminary results are presented that demonstrate the sensitivity, selectivity, and reproducibility of this method. Detection limits of 2.0 ppm for CO, 2.5 ppm for CO₂, 1.8 ppm for H₂O, 19.4 ppb for NH₃, 7.9 ppb for HCN, and 4.0 ppb for C₂H₂ are calculated³².

CRS is not yet at a sufficient Technology Readiness Level to be considered for use in combustion products monitoring.

4.0 RECOMMENDATIONS

A research and development effort is required to meet NASA's requirements for post-fire gas detection. Laser absorption spectroscopy offers much promise for this application. Solid-state electrochemical sensors are also attractive due to their small size and low cost.

As of September 2010, the VIS/IR technologies appeared to have much better specificity (much lower probability of confounding detection that could lead to false positives or false negatives), but technical readiness was not high enough for short-term inclusion on an upcoming flight. Electrochemical and solid state detectors suffered from drift, lack of internal calibration, and serious lack of specificity, including pathological cases in which one gas would counteract the detection of CO.

Recommendation 1: Hybrid Sensor Systems and Arrays

A hybrid sensor system that uses a multimodal approach incorporating several sensing elements and produces data that are multivariate in nature is another attractive approach for detection in complex backgrounds. Several examples of hybrid detection systems have been used for fire detection on Navy ships³³. Though a hybrid sensor is itself an array, hybrid sensors are often organized into more complex sensing systems. Part of the reason for the shift to hybrid sensors is a result of advancements in sensor technology and availability of computational power for processing larger amounts of data. However, the benefits of a multisensory approach are not automatically achieved. Interpretation of data from hybrid arrays of sensors requires a methodology to optimally fuse the disparate sources of data generated by the hybrid array into useful information characterizing the sample or environment being observed. Consequently, multivariate data analysis techniques such as those employed in the field of chemometrics have become more important in analyzing sensor array data. Depending on the nature of the acquired data, a number of chemometric algorithms may prove useful in the analysis and interpretation of data from hybrid sensor arrays.

No "electronic nose" or similar technology was presented. In the past, these architectures have included numerous, less-specific transduction elements, but there is no reason that such an instrument could not include both "specific" solid-state or electrochemical transducers along with the less-specific ones. Clearly, this would require some effort to create. If such an electronic nose were included as part of a mission for non-combustion-sensing applications, it would still be valuable to include it in testing challenge mixtures in order to improve the signature capability of any data-fusion algorithms.

Recommendation 2: Data Fusion

There is also ample evidence to support the claim that a multivariate analytical approach is generally superior to univariate measurements, because it provides additional redundant and complementary information³⁴. Emergency scenarios where fire incidents produce combustion products outside the detection envelope of a targeted optical sensor may result in exposure of personnel to other gases not anticipated in the original analyte panel, with unknown toxicological effects. Data fusion methods combined with hybrid sensor arrays using a multicriteria approach is an attractive method for complex mixtures. Such systems can be used to extrapolate to unknowns and can identify classes of chemicals.

Recommendation 3: Field Trials

The majority of the panel felt that testing multiple instruments and types of instruments with complex mixtures would be an important reality check for confounding factors, sensitivity, and specificity.

NASA should make known the nature of the test mixtures of interest to them. It is easy to envision scenarios in which unknown and/or unexpected vapors could be produced, not just due to equipment overheating, but also due to metabolic and by-product gases from microbes and even from the crew. It may be challenging to create relevant challenge mixtures for testing instruments. Nonetheless, simply asking the manufacturers if their instruments can detect low concentrations of pure target gases is necessary but not sufficient to establish the value and reliability of combustion-sensing instruments.

Recommendation 4: Dedicated Calibration Facility

The replacement CPM has a desired measurement range and resolution for specific analytes. These analytes are components of fire smokes and/or thermal degradation products. Calibration of the device to diluted compounds or mixtures is necessary to provide accurate readings. In addition, the performance of a replacement CPM needs to be verified by exposure tests with real fire smokes. The complex mixture of gases and particulates in fire smokes may challenge the replacement CPM by producing false high or low readings, poison sensors, or otherwise irreversibly damage the device, or may identify the need for accelerated calibration after smoke exposure.

A calibration facility that can expose the device to controlled concentrations of compounds and mixtures would verify accuracy, measurement range, and resolution. Such a facility could also be used to investigate cross-sensitivities of sensors and instruments to specific compounds that may co-exist with the analyte of interest. Cross-sensitivity to a particular compound is sensor-specific. Exposure tests to real fire smokes like those conducted at the White Sands Test Facility could be used to identify cross sensitive compounds generated in sufficient quantity with respect to the target analyte. A cross-sensitivity to a compound potentially present with the analyte does not necessarily exclude that sensor technology. However, quantification of the cross-sensitivities is needed to estimate the uncertainty in the combustion products monitor readings so that appropriate conservative judgments can be made.

Recommendation 5: Mass Spectrometry

The specifications for combustion instrumentation seem to have precluded GC-MS instruments, but it is recommended that one be included onboard as a general-purpose analytical instrument, for reasons discussed in Section 3.1 above.

APPENDIX A: INFORMATION FOR PRESENTERS

Combustion Products Monitor Operational Concept

The CPM will be used on the ISS during and after a combustion event to monitor cabin concentrations of marker compounds of the combustion process and to help crew locate a combustion event within a rack (see *Combustion Products Monitor Operational Concept*, page 2) if no visual nor computer indication is available. In addition to combustion events, the CPM may be used by crew as a means to “check” the atmosphere in areas of the vehicle where the air is suspect. The current CPM on ISS is the Compound Specific Analyzer – Combustion Products (CSA-CP). The CSA-CP employs three electrochemical sensors to detect and quantify carbon monoxide (CO), hydrogen cyanide (HCN), and hydrogen chloride (HCl). A fourth electrochemical sensor for oxygen (O₂) is present but is not used during a combustion event. There are four CSA-CP units on-orbit located throughout the ISS and they will continue to be used until 2014. Characteristics and specifications of the CSA-CP can be found in *The Current Combustion Products Monitor*, page 3.

The primary purpose of the CPM is to monitor the ISS cabin atmosphere for the presence of fire products (CO, HCN, and HCl) during and after a fire event and for fire location within the racks in the US On-Orbit Segment (USOS) modules. Fire location requires the use of an external probe for sampling behind the front panel of each rack through rack fire ports. It should be noted that crew members have also employed the CPM as a means to check the “breathability” of the atmosphere crew member believe to be suspect (usually indicated by an odor) in various areas of the ISS. The current, portable hand-held CPM allows for this somewhat limited “quick check”.

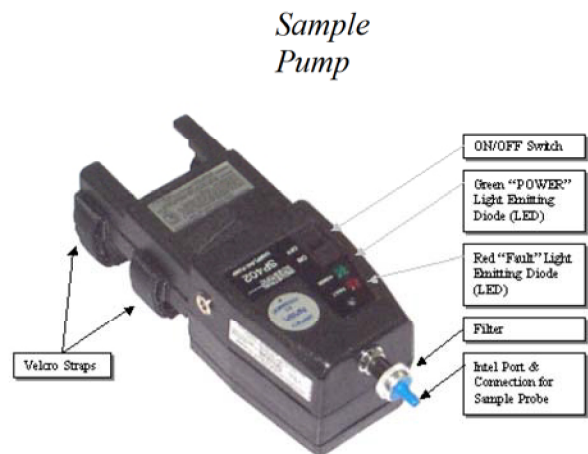
The following general approach to a fire event in the USOS illustrates how the CPM will be employed:

1. If visible flames, smoke, or crew discretion (burning odor): crew activates fire alarm if not already triggered by fire detection system.
2. Crew collects emergency equipment (breathing masks, CPMs, flashlights), don masks if needed, and gather at pre-defined central location. Need for breathing masks is determined by CP monitor or at crew discretion.
3. If burning odor observed, locate source and attempt to remove local power, check atmosphere for levels of fire products with CPM.
4. If no visible indication of fire, attempt to locate fire with PCS (portable computer system) and remove local power.
5. If fire location within module unknown (via odor or PCS), perform fire source location within module with CPM.
 - a. Activate CPM.
 - b. Sample module atmosphere to obtain background levels.
 - c. Insert sample probe into fire port of rack to obtain reading.
 - d. Sample module atmosphere to reset the sensors before going to next fire port.
 - e. Continue until fire source located and verified.
 - f. FIRE CONFIRMED if CO level is 10% above background or >500 ppm.
6. When fire located, remove local power from rack, and sample for 5 minutes recording CO levels every 30 seconds.
 - a. If CO level continues to increase, discharge portable fire extinguisher into fire port, egress module and close hatch, and continue to post-fire clean-up.

- b. If CO levels decrease, egress module, and continue to post-fire clean-up.
7. Post-fire, ingress module with mask and check cabin atmosphere with CPM and carbon dioxide monitor.
8. Assess module and deploy required atmosphere scrubbing assets.
9. Monitor atmosphere with CPM and carbon dioxide monitor as needed.
10. Once clean-up is complete, re-enable smoke detectors in module.

The Current Combustion Products Monitor:

CSA-CP Compound Specific Analyzer – Combustion Products



Advantages of the Current ISS Combustion Products Monitor (CSA-CP)

1. Addresses the high-value CP targets (CO, HCN, HCl) plus O₂ in acceptable concentration ranges
2. On-orbit performance has been excellent, both for routine and contingency analysis.
3. Compact, dense, explosion-proof hand-held unit with a pump/probe attachment for detection of event behind racks through the fireholes.
4. Commercial Off-the Shelf (COTS) and, therefore, relatively inexpensive.
5. Units can be zeroed on orbit by use of hopcalite cartridge (consumable).
6. Crew is comfortable with CSA-CP and uses them frequently (although they complain about monthly zeroing)

Disadvantages of the Current ISS Combustion Products Monitor (CSA-CP)

1. Obsolescence: the current CSA-CP unit is no longer manufactured; NASA has several dozen to supply ISS for 2 to 3 more years. A new model is available, but the changes are sufficient that recertification for use on ISS would be necessary.
2. Battery management is problematic. Crew calls down “battery ticks or bars” and frequently swaps battery packs; there is no capability for inflight recharge. Four units must be maintained in operational state on ISS.
3. Unit has a relatively dark display (old technology), difficult to see the decimal point. Numbers are not written in a 0.X data format.
4. No built-in pressure compensation.
5. ISS usage restrictions: CSA-CP cannot be used in the airlock and must be used in pairs for critical measurements because of failure modes.
6. Sensor calibration life limits use of each unit to ~ 6 months in flight.
7. When supplying new units in kits, the unwrapped units must be “aired out” for 2 to 5 days before entering service, to alleviate self-contamination of the sensors.
8. Manufacture of the electrochemical sensors is not a real batch mode process and sensor performance has been seen to be affected by small changes in manufacturing processes.

CSA-CP Characteristics*								
Mass	Vol	Dimension	Active Sampling	Battery Life	Battery Type	Sensors	Data Logging	Zeroing On-orbit
0.6 kg (1.3 lb.)	432 cm ³ (26 in. ³)	12.1 cm × 7 cm × 5.1 cm (4.75" × 2.75" × 2.0")	Yes (external pump)	720 hrs (passive ops)	Lithium	CO, HCN, HCl, O ₂	110 hrs	Yes

Sensor Detection Limits and Noise*				
Sensor	Exposure Concentration	Sensor Response (n=8)	Sensor Noise (n=8)	Display Resolution
CO	3 ppm	2 ppm	±1 ppm	1 ppm
HCN	0.4 ppm	0.3 ppm	±0.1 ppm	0.1 ppm
HCl	0.4 ppm	0.1 ppm	±0.0 ppm	0.1 ppm
O ₂	5.0%	5.0%	±0.1%	0.1%

Measurement Parameters / Analysis Capabilities*				
Sensor	Linear Operating Range	Detection Limit	Response Time (Baseline to 80% Maximum Response)	Recovery Time (Maximum Response to 20% Above Baseline)
CO	3 – >400 ppm	3 ppm	<1 min	<1 min
HCN	0.4 – 30 ppm	0.4 ppm	<3 min	<3 min
HCl	0.4 – 30 ppm	0.4 ppm	<3 min	<3min
O ₂	5 – 30%	5%	<1 min	<1 min

*Reference: Limero, T.; Beck, S.W.; and James, J.T. *The Portable Monitor for Measuring Combustion Products Aboard the ISS*. ICES2002-01-2298, Society of Automotive Engineers: Warrendale, PA, 2002.

DESIRABLE SPECIFICATIONS FOR A COMBUSTION PRODUCTS MONITOR

Workshop participants are asked to speak to the following desirable characteristics for a Combustion Products Monitor, and to discuss how well their technology meets these characteristics and/or what it would take to develop the capability to meet them.

1.0 PHYSICAL DESIRABLES

1.1 Volume

The instrument should not exceed a total volume of 100 cubic inches (1638 cm³).

1.2 Weight

The instrument should not exceed 15 pounds (6.8 kg) at the kit level.

2.0 GENERAL INSTRUMENT DESIRABLES

2.1 Alarm Indication

The instrument should provide both audio and visual alarm indicators that annunciate when gas concentrations exceed preset threshold levels.

2.2 Battery Operation

The instrument should utilize rechargeable batteries for operation.

3.0 PERFORMANCE DESIRABLES

3.1 Analytes

The instrument should be capable of monitoring the following analytes in the specified range and resolution:

Compound	Measurement Range	Resolution
HX*	0.4 – 30 ppm**	0.1 ppm
O ₂	14 – 32%	0.1%
CO ₂	0.05 – 3.0%	0.1% (0.01% below 0.1%)
CO	0 – 500 ppm	1 ppm
HCN	0.4 – 30 ppm	0.1 ppm

*HX denotes the total concentration of halide acid gases HF, HCl, and HBr. If a total halide acid gas cannot be provided, then the order of preference is the following: HF, HBr, HCl.

** ppm is parts-per-million at 1 atm

3.2 Useful Life

A useful life, including sensor calibration life, of 1 year or greater is highly desirable.

3.3 Analyte Tracking

Ideally, the sensor will follow the entire event from onset through cleanup without fouling.

COMBUSTION PRODUCTS MONITOR DRAFT REQUIREMENTS

These draft requirements are based on the current requirement to monitor the concentration of CO and HCN in case of a fire and experience using the CSA-CP over the past several years.

Workshop participants are asked to speak to these requirements and to discuss how well their technology meets these characteristics and/or what it would take to develop the capability to meet them.

1.0 INTERFACES WITH THE ISS

The physical and functional interfaces shall conform to the requirements in SSP 42014, *Crew Health System (CHeCS) to Lab Interface Control Document*.

- 1.1 Mounting Interface
Instrument shall provide a means of mounting to Velcro in the Space Station modules.
- 1.2 Rack Interface
Instrument shall provide a means of active sampling air internal to an ISS rack via a rack firehole (probe required).
- 1.3 Data Interface
The instrument shall communicate with the onboard laptop computer, i.e., the Medical Equipment Computer (MEC), either wirelessly (desirable) or through other means for downloading of data stored in the data logger. Scar the system for wireless (future expansion).

2.0 PHYSICAL REQUIREMENTS

- 2.1 Portability
The instrument shall be a portable device, ideally hand-held.

3.0 GENERAL INSTRUMENT REQUIREMENTS

- 3.1 Instrument Display
The instrument shall display the following: analyte and concentration, power on/off indication, battery level/status indicator, and low-flow status when active sampling.
- 3.2 Data Storage Requirements
The instrument shall be capable of storing all analyte concentration data time stamped at 1 min. intervals for at least 1 day.
- 3.3 Operating Pressure Range
The instrument shall perform as specified herein in a pressure environment of 0.945 atm (13.9 psia) to 1.014 atm (14.9 psia). No ground data correction shall be required.
- 3.4 Operating Humidity Environment
The instrument shall meet the functional performance requirements specified herein when exposed to an operating range of 20 to 80% relative humidity (RH).

3.5 Alarm Indication

- a. The instrument shall not induce an erroneous audio or visual indication due to a pressure change in a variable pressure environment from 0.680 atm (10 psia) to 1.034 atm (15.2 psia).
- b. Visual alarm indicators shall be provided for low sample flow (active mode), low battery, and failed battery.

3.6 Battery Operation

- a. The instrument shall be portable and capable of operating while powered from batteries for a period of 4 hours in an active sampling mode. Active mode is defined as airflow forced over the sensors.
- b. The instrument shall be designed with features to allow simple on-orbit replacement of the batteries without specialized tools.
- c. The instrument shall remain in calibration after a battery failure.

3.7 Fireport Sampling

The instrument shall provide a means of active sampling of air through a firehole or through interface with an ISS rack.

3.8 On-Orbit Zeroing or Calibration

On-orbit zeroing and/or calibration of the sensors or device shall be provided as appropriate to the technology. The zeroing capability may be provided by means of a filtering device to remove combustion/analyte products (CO, HCN, HX) from the air being pumped through it. The use of a consumable calibrant gas is highly undesirable.

3.9 Extended Operation

The instrument shall be designed to operate continuously utilizing ISS power or, alternatively, operate for a period of 18 days utilizing installed battery power.

3.10 Consumables should be minimized. Consumables include calibrant gases, reagents, filters, or anything else which is discarded after use. If a consumable is unavoidable, it should be reusable several times.

4.0 PERFORMANCE REQUIREMENTS

4.1 Analytes

The instrument shall be capable of monitoring the following analytes in the specified range and resolution:

Compound	Measurement Range (ppm*)	Resolution (ppm)
CO	0 – 500	1
HCN	0.4 – 30	0.1

* ppm is parts-per-million at 1 atm

- 4.2 Analyte Accuracy Within 24 Hours Post-Calibration
CO: 40 ppm \pm 5 ppm; 500 ppm \pm 30 ppm
HCN: 10 ppm \pm 2 ppm; 20 ppm \pm 4 ppm
- 4.3 Analyte Accuracy Within 15 months Post-Calibration
CO: 40 ppm \pm 10 ppm; 500 ppm \pm 50 ppm
HCN: 10 ppm \pm 3 ppm; 20 ppm \pm 6 ppm
- 4.4 Analyte Response and Recovery Times
CO: Sensor shall reach 80% of the steady-state response within 30 seconds and shall recover (80%) from the exposure within 30 seconds. The steady-state response for the CO sensor is defined as ≤ 3 ppm change over a 20 second period for the 500 ppm test gas exposure and ≤ 1 ppm change over a 20 second period for the 50 ppm test gas exposure.
HCN: Sensor shall reach 80% of the steady-state response within 1.5 minutes and shall recover (80%) from the exposure within 1.5 minutes. The steady-state response for the HCN sensor is defined as ≤ 0.2 ppm change over a 20 second period.
- 4.5 Useful Life
The instrument useful life shall be no less than 15 months from the date of sensor calibration.
- 4.6 Analyte Tracking
The instrument shall have the demonstrated ability to accurately measure and follow analyte concentrations as they decrease in a complex matrix of combustion products.

APPENDIX B: CHARGE TO PANELISTS

The CP Panelists are charged to compare and evaluate the various technologies presented and assess the applicability of each technology to ISS as the next combustion products monitor based on “Desirable Specifications for a Combustion Products Monitor” and “Combustion Products Instrument Draft Requirements” of the information document titled *CP Monitor Workshop* (see Appendix A of this document). Reviewers are asked to use the ISS as the primary frame of reference for evaluating candidate sensors and instruments.

Each presenter has been asked to fill out the table at the end of the information document with characteristics of the technology and device they are discussing. If they are in the process of development, presenters will also fill out a table with characteristics which can be reached in 2 to 3 years. This table will be filled out for the current CSA-CP and provided to you at the workshop.

Some of the characteristics are highly sensor-dependent, such as the need for replacement units, consumables, and any additional hardware required for replacement or repair of the unit; all of these add to the overall mass and volume requirements for a given sensor. The amount of crew time involved in set-up, calibration, operation, replacement of consumables, sensor repair and/or replacement, and the frequency of those activities is also an important consideration.

Panelists can provide the most benefit by not only ranking the candidate sensors in terms of their current capability, but also by identifying gaps and pointing out near-term development path(s) as remedies. This guidance may include identifying performance improvements that could be achieved with additional investment, as well as potential risks or roadblocks to improving sensor and system performance.

Desired performance improvements over the current Combustion Products Monitor include increased sensitivity; improved accuracy and stability; increased lifetime; reductions in crew-time required for operation, repair or replacement; decreased mass, power, and/or volume; and decreased cost of the flight-qualified-sensor. Potential roadblocks range from fundamental limitations of the sensor physics to a drastic, and therefore expensive, re-design required to achieve a flight-qualified sensor. The list of flight sensor characteristics listed in the table can be considered in terms of either improvements or roadblocks.

APPENDIX C: REFERENCES

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